

## METHOD FOR MONITORING SURFACE TREATMENT OF COPPER CONTAINING DEVICES

## FIELD OF THE INVENTION

The present invention relates generally to the field of operations taking place during the manufacturing of copper-containing microelectronic devices. In particular the present invention relates to qualitative determination of the effectiveness of removing certain residual components from cleaning steps during manufacturing of microelectronic devices.

## BACKGROUND OF THE INVENTION

The present day fabrication of semiconductor devices is a complex, multi-step process. Such processes involve a multiplicity of steps starting with a particular substrate and layering various device configurations one on top of the other. In between each of the successive layering steps the devices may be subject to a cleaning step. In particular, when the surface to be cleaned contains copper, copper surfaces or copper wire connects a cleaning solution containing a corrosion inhibitor is generally used to prevent corrosion of the copper during the cleaning step. When such corrosion inhibitor is a beta triazole (BTA) which is commonly used

during the fabrication of microelectronic devices containing copper connects or copper surfaces the corrosion inhibitor must be removed prior to a subsequent manufacturing operation.

As part of normal cleaning step the cleaning solution is usually rinsed  
5 from the surface of the microelectronic device using the deionized water followed by a drying step. If the cleaning solution is not removed from the surface subsequent manufacturing steps may be effected and the device may not meet the required specification, thus resulting in a high volume of rejected devices.

#### SUMMARY OF THE INVENTION

10 The present invention is a method for detecting the presence of a residual amount of corrosion inhibitor on a copper surface subjected to a cleaning solution containing a corrosion inhibitor by exposing the copper surface to a reactant that will react with the copper surface causing a pronounced color change of the copper surface, the color change indicating absence of corrosion inhibitor on the  
15 cleaned copper surface. As a feature of the invention the method can include using a sacrificial test piece or coupon that is subjected to the cleaning operation along with the semi-conductor device being fabricated. The test piece or coupon is then subjected to contact with a gaseous reactant. If the test coupon surface is devoid of residual corrosion inhibitor the surface will change color, the color change indicative  
20 of the absence of corrosion inhibitor on the devices being fabricated.

Therefore, the present invention is a method for determining the presence of residual corrosion inhibitor on a copper surface or copper components of

a microelectronic device having been subjected to a cleaning operation prior to a subsequent fabrication operation comprising, including a sacrificial copper coupon or test piece in a group or batch of the devices during the cleaning process, removing the test piece from the batch after the cleaning step is completed and exposing the test piece to a reactant selected to react with the test piece to produce a visible color change on the surface of the test piece, wherein the color change of the surface indicates presence or absence of a residual corrosion inhibitor on the test piece and the components being processed.

#### BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic representation of a test method according to the present invention illustrating a first step in the method of the present invention.

Fig. 2 is a schematic representation of the completion of the method of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

Referring to Fig. 1 the apparatus of the invention 10 includes a first small beaker 12 (e.g. 100 milliliter capacity) which contains a solution 14 consisting of 2% sodium sulfide and deionized water. The solution 14 can be prepared by dissolving 1 gram of sodium sulfide and 49 grams of deionized water at room temperature. The 100 milliliter beaker 12 is placed in the bottom center of an upright two (2) liter beaker 16. Test pieces of copper 18 are placed on the bottom of the two (2) liter beaker 16 surrounding the 100 milliliter beaker 12. By means of a

pipette or other dropper device 20, one (1) milliliter of acetic acid 22 is added to the sodium sulfide solution 14 in the small beaker 12. The two (2) liter beaker is then covered by a four (4) liter beaker 24 as shown in Fig. 2 to contain hydrogen sulfide gas 26 which is produced by the reaction of the acetic acid 22 and the sodium sulfide solution 14. The test pieces 18 are treated for two (2) minutes by hydrogen sulfide gas coming out of the small beaker 12 and falling to the floor of the two (2) liter beaker 16 thus attacking the test pieces 18 uniformly. The entire experiment or test must be carried out under suitable chemical evacuation hoods so that the hydrogen sulfide gas does not enter the work space and can be effectively scrubbed from the atmosphere. The reason for using the large beaker inverted over the mid-size beaker is to prevent the effect of hydrogen sulfide gas being evacuated from the fume hood instead of attacking the test pieces 18, as would be the problem with beaker 16 not being covered since the hydrogen sulfide gas would be drawn into the fume hood and not fall onto the test pieces 18.

According to the process of the invention adding the acetic acid to the 2% sodium sulfide solution lowers the pH of the basic solution to approximately 4.8. This reaction releases hydrogen sulfide gas, which is heavier than air. By placing the test pieces in an area surrounding the small beaker the gas will react with the copper on the test pieces. The reaction is visible by a change in the color of the copper on the test pieces. Areas of the wafer that are still protected by the corrosion inhibitor (BTA or any other copper protecting chemical) will not change color.

During the first 30 seconds, copper oxidation begins to occur and continues throughout the treatment. A treatment time of two (2) minutes was chosen to thoroughly expose to copper test pieces while at the same time causing

little or no color change to any pieces that contain a surface covered with the corrosion inhibitor. At longer treatment times hydrogen sulfide will begin to react with the corrosion inhibitor, especially those pieces treated with beta triazole (BTA).

Comparative tests were run to test the method of the present invention. In one test a copper wafer was cleaned in a solution containing 10 ppm of BTA. The test pieces were exposed to the cleaning solution for two hours at 22°C and rinsed in for 30 seconds in deionized water followed by a drying treatment using dry nitrogen gas. The test pieces thus prepared and test pieces without exposure to the cleaning solution were subjected to the process of the present invention. Those that were devoid of BTA turned a deep blue color after exposure to the hydrogen sulfide gas, indicating a complete removal of the BTA. In those instances where the BTA was not completely removed the copper surface did not change color and retained a reddish color throughout.

Experimental results also showed that in addition to acetic acid other acids such as citric, ascorbic, hydrochloric and sulfuric can be mixed with a sodium sulfide solution to generate hydrogen sulfide gas. In any event in order to generate sufficient hydrogen sulfide gas the acid must be added in sufficient quantity to lower the pH of the acid/sulfide solution to below 8.

Prior to the present invention one way to determine whether or not beta triazole (BTA) or some other corrosion inhibitor is present on a copper surface was to submit samples or a test sample suspected of having corrosion inhibitor on the surface to X-ray Photon Spectroscopy (XPS) or Time Of Flight Scanning Ion Mass Spectroscopy (TOF-SIMS).

The present invention provides a quick and inexpensive qualitative method to determine whether or not any corrosion inhibitor is left on exposed copper surfaces. The method of the invention is used to determine if a cleaning regime has resulted in the removal of corrosion inhibitor so that the microelectronic devices can  
5 be moved to the next process step. Using a sacrificial strip or test piece placed with the devices being cleaned it is possible to determine whether or not the cleaning step is effectively completed without sacrificing any of the devices being processed, or subjecting any of the devices being processed to complex analytical techniques.

The process of the present invention can also be used to determine  
10 whether or not new cleaning formulations with corrosion inhibitors are effective or can be effectively removed from the microelectronic devices at the required stages during manufacture of a device.

Having thus described our invention what is desired to be secured by Letters Patent of the United States is set forth in the appended claims.